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The Valence of Iodine in Nitrogen Iodide



THE VALENCE OF IODINE IN NITROGEN IODIDE

BY

CARL PETER MOYEN

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

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---

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1917

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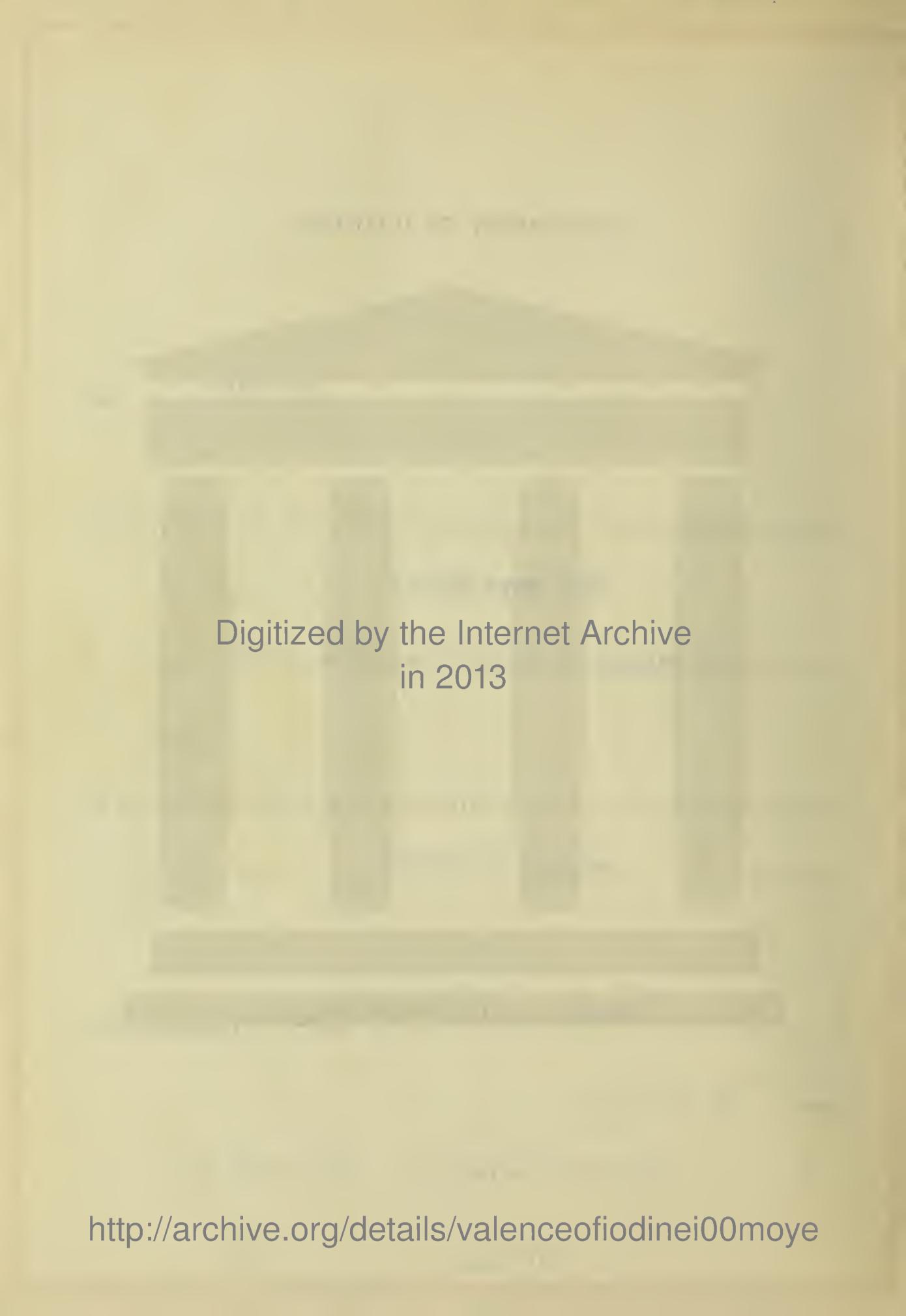
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## THE VALENCE OF IODINE IN NITROGEN IODIDE.

### INTRODUCTION.

The primary object of this thesis is to determine the valence of Iodine in the so-called Nitrogen Iodide in order to throw more light upon the structure of that compound and perhaps locate the reasons for its peculiar instability. The work has mainly been carried on in two parts. First to verify and check the work of previous investigations on the subject, and second: to produce compounds related in structure to Nitrogen Iodide with the molecule so loaded as to produce a greater stability.



Probably the most extensive of the past investigations upon the subject of nitrogen iodide has been done by F.D.Chattaway with the assistance of K.J.P.Orton and H.P. Stevens. These men have made an exhaustive research on the problem and have accumulated a vast amount of quantitative data and analyses on the reaction of nitrogen iodide under numerous conditions with many reagents. Among their work on the subject appears,

"THE PREPARATION AND PROPERTIES OF THE SO-CALLED

NITROGEN IODIDE." by F.D.Chattaway & K.J.P.Orton (1.)

Under this title appears a brief review of how the compound was prepared previous to their investigation, their methods of preparing both the amorphous and crystalline compound, the general properties of the same and a brief description of the crystals of this compound as determined by W.J.Pope.

"THE ACTION OF REDUCING AGENTS UPON NITROGEN IODIDE"

by F.D.Chattaway & H.P.Stevens (2.)

This investigation takes up the action of the following reducing agents,  $\text{Na}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{SnCl}_2$  and  $\text{H}_2\text{S}$ , giving the results produced by each upon nitrogen iodide in detail. Also considerable analytical data is given to substantiate their statements completely. The following table shows the relative reducing power of each of the agents used.

am't reducing agent oxidized.	$\text{Na}_2\text{SO}_3$	$\text{H}_2\text{SO}_3$	$\text{As}_2\text{S}_3$	$\text{Sb}_2\text{O}_3$	$\text{SnCl}_2$	$\text{H}_2\text{S}$
am't of HI						
simultaneously produced.	HI	HI	2HI	2HI	HI	HI

(1.) refer to Am.Chem.J. 23, 363, (1900)

(2.) refer to Am.Chem.J. 24, 139, (1900)



All iodine contained in nitrogen iodide, therefore behaves toward reducing agents like the chlorine contained in a hypochlorite and exerts twice its normal oxidizing power. Normal probably meaning that generally associated with the element.

"THE COMPOSITION OF NITROGEN IODIDE" by F.D.Chattaway.(1.)

A brief resume of the properties of nitrogen iodide and its general composition is discussed being followed by considerable experimental data with a discussion of the analytical results obtained. Experiments were also made to determine whether similar substances of composition differing from  $N_2H_3I_3$  could be produced. Nitrogen iodide was prepared in the following ways and analyses are given to show the degree of purity and consistancy of the compounds obtained.

- (1) Thru the action of a solution of iodine in potassium iodide on a solution of ammonia. The average nitrogen, iodine ratio for 6 analyses is 1.998 : 3.
- (2) From the action of a strong ammonia solution on solid iodine. Average ratio for 6 analyses 1.983 : 3.
- (3) Thru the action of an alcoholic solution of iodine upon ammonia. Average ratio for 6 analyses 1.987 : 3.
- (4) By adding ammonia to a solution of potassium hypoiodite containing an excess of potash. Average ratio for 6 analyses 1.997 : 3.
- (5) From the action of iodine monochloride on ammonia. Average ratio for 6 analyses 1.995 : 3.

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(1.) refer to Am.Chem.J. 24, 139, (1900)



(6) The action of bleaching powder on ammonium iodide.

Average ratio for 3 analyses 1.990 : 3.

Analyses of amorphous nitrogen iodide dried over baryta in an atmosphere of ammonia, light being totally excluded. The following figures are averages of 8 analyses of the dried compound.

<u>nitrogen, iodine ratio</u>	<u>% iodine</u>	<u>% nitrogen</u>
1.993 : 3.	92.42	6.81

The weights of the dry samples varying from 0.2733 to 0.5937 g. All attempts to prepare similar substances of composition differing from  $N_2H_3I_3$  seem to have failed as their accompanying analytical data shows that the nitrogen, iodine ratio always varied closely around the 2 : 3 figure. The nitrogen value ranging from 1.98 to 2.006. Mixtures of any composition from nitrogen iodide to pure iodine were prepared by washing the pure compound continuously with distilled water. As a final summation of his investigation, it seems only quite evident that the simplest formula that nitrogen iodide can have is  $N_2H_3I_3$ .

#### "THE ACTION OF LIGHT ON NITROGEN IODIDE"

by F.D.Chattaway & K.J.P.Orton (1.)

The experimental portion of this subject is also preceded by a brief review of this portion of the subject touched upon by others, with a description of the action of light upon nitrogen iodide. An estimation of each substance produced, when nitrogen iodide suspended in a solution of ammonia decomposes under the influence of light is given; being accompanied by analytical data to show the accuracy of the results obtained.



The article also includes a demonstration with analytical data, to show that hydriodic acid is liberated during the decomposition by light. The observed action of light on iodine suspended in a solution of ammonia, being followed by the action of light of different wave lengths on nitrogen iodide. The results of this last determination show that the decomposition produced varies directly with the wave length. White, red, green, blue and indigo lights were tried. The red end of the spectrum producing decomposition most readily being followed by the blue as a second maximum. The final statement being made that nitrogen iodide under the action of light, decomposes quantitatively into nitrogen and hydriodic acid.

"THE ACTION OF ALKALINE HYDROXIDES OF WATER AND  
HYDROGEN PEROXIDE UPON NITROGEN IODIDE"

by F.D.Chattaway & K.J.P.Orton

(1.)

Under this topic the reactions of nitrogen iodide with the following are given, potassium hydroxide, water and hydrogen peroxide. For the reaction with potassium hydroxide, the following reaction is given;



At the same time a portion of the compound always breaks down under the influence of light to nitrogen and hydriodic acid.



These statements are backed with analytical results to show that nitrogen iodide under these conditions, acts according to

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(1.) refer to Am.Chem.J. 24, 318, (1900)



the predictions. To show that equation 2 actually takes place, results on analyses carried on in the presence and absence of light are compared.

Under action of water, nitrogen iodide breaks down as follows,

$$\text{N}_2\text{H}_3\text{I}_3 \longrightarrow 2 \text{ NH}_3 + 3 \text{ HOI}$$
$$\text{N}_2\text{H}_3\text{I}_3 \longrightarrow \text{N}_2 + 3 \text{ HI}$$
$$\text{HI} + \text{HOI} \longrightarrow \text{I}_2 + \text{H}_2\text{O}$$

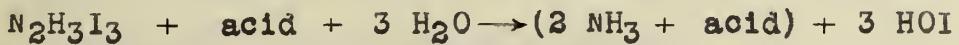
This statement and equations are also followed by positive analytical results.

The action of hydrogen peroxide alone and in the presence of potassium hydroxide on nitrogen iodide is given. The authors stating that the process is essentially one of hydrolysis. Potassium hydroxide is used in one case to prevent the deposition of solid iodine. Analytical results of sufficient importance to be convincing are given.

#### "THE ACTION OF ACIDS UPON NITROGEN IODIDE"

by F.D.Chattaway & H.P.Stevens. (1.)

A brief description of the general behavior of nitrogen iodide towards acids is given, and is followed by the actions of specific acids upon the same, including experimental data. The acids considered are hydriodic, hydrocyanic, sulfuric, phosphoric, acetic and hydrochloric. Step equations being included to more clearly express the reactions produced by the more important ones. The general equation for the action of acids upon nitrogen iodide is given as,

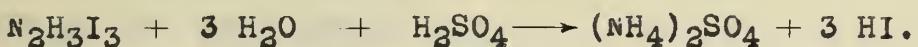


Further reaction depending on the nature of the specific acid



used. When hydriodic acid is used, ammonium iodide is formed and iodine is liberated thru the action of the HI on the hypoiodous acid formed. If light be excluded completely, no nitrogen will be evolved. The statement is made that the iodine contained in  $N_2H_3I_3$ , behaves as if it were first liberated as HOI. This being followed by complete analytical data. As a conclusion from the results, the authors say that nitrogen iodide entirely hydrolyses into hypoiodous acid and ammonia.

Under the reaction of sulfuric acid on  $N_2H_3I_3$ , the formula of that acid is inserted in the general acid equation. The authors are quoted in saying, "the nitrogen and hydriodic acid formed thru direct decomposition, do not prevent an estimation of the ammonia and the hypoiodous acid formed thru the hydrolysis. Such an estimation shows that these compounds are formed in proportion required by the second equation."



These statements are all followed by analytical results.

#### "THE FORMATION AND CONSTITUTION OF NITROGEN IODIDE"

by F.D.Chattaway & K.J.P.Orton.

(1.)

This is the last of the papers published by the mentioned investigators. In this closing article, we find a concentrated summary of the results obtained in the previous publications. Among the final conclusions of these investigators, we find:

The oxidizing reaction of nitrogen iodide represented as



where R stands for any reducing agent.

Under all observed circumstances, nitrogen iodide shows a

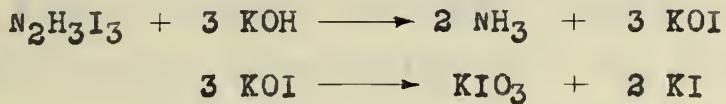


tendency to break down thus,



Under the action of light this decomposition takes place with great rapidity and there is but little doubt that in the explosion of the dried compound that a similar decomposition takes place.

Under the action of alkalies and acids, two separate reactions take place committantly, hydrolysis and a decomposition into nitrogen and hydriodic acid. For alkalies the following equation is offered,



For acids,



The final products of the acid reaction being determined by the nature of the acid used.

These reactions leave no doubt that in nitrogen iodide, neither the iodine nor the nitrogen is present in loose molecular combination as occurs in peri- or acid iodides. Experimental data is also included which gives the action of iodine on a solution of ammonia, ammonia on a solution of potassium hypoiodite and ammonium hydroxide on nitrogen iodide. This is followed by a study of the various stages in the decomposition of nitrogen iodide by water and also dilute sulfuric acid. In speaking of the action of dilute sulfuric acid, as a closing statement, the authors are quoted in saying; "It is seen that the ratio of the nitrogen to the iodine atoms in the residue, excluding the free element (iodine), continually decreases as the decomposi-



tion proceeds and it slowly approaches the ratio N : 3I required by the substance  $\text{NI}_3$ . This result makes it very probable that the constitution of the molecule really is represented by the formula given above ( $\text{NH}_3 ; \text{NI}_3$ ), and that on decomposition by water or dilute acids, those molecules which do not break down into  $\text{N}_2$  and  $\text{HI}$ , first decompose into  $\text{NI}_3$  and  $\text{NH}_3$  and that the former is then hydrolysed.

If the ratio N : 3I could be ultimately obtained, and the results were absolutely to be relied upon, the formula would be established. The large percentage of iodine present, when the ratio is nearly reached, introduces, however, a possibility of error, and altho the constitution  $\text{NH}_3 : \text{NI}_3$  is rendered very probable, it cannot be regarded as conclusively proved.

#### Discussion of Results.

The following conclusions are drawn from the work previously explained, checked and discussed, considering the results obtained from an electrostatic standpoint of charges within the molecule of nitrogen iodide.

From the decomposition of nitrogen iodide, thru the action of light, the equation is as follows,



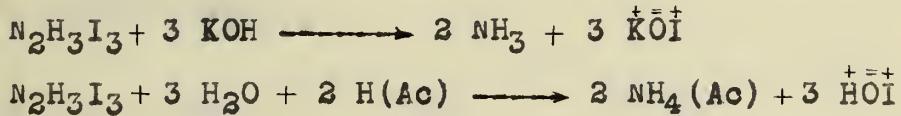
The final product of the total iodine being hydriodic acid, within the molecule of which the iodine possesses negative static charges. From this an electrostatic formula may be expressed thus,





According to this formula the iodine contained within the molecule bears negative charges, the first nitrogen atom bearing four negative and one positive charges similar to that contained in ammonium iodide, while the second atom of nitrogen holds the charges reversed being similar to the nitrogen contained in nitric acid. But according to the latest theories of Physics, light is thought to be probably an electromagnetic phenomenon; which is more apt to be accompanied by electrostatic changes within the molecule. If, however, this be the case, then the decomposition of nitrogen iodide by light possibly indicates that the combined iodine within the molecule bears positive electrostatic charges.

In both the decompositions of nitrogen iodide by acids and alkalies, which are essentially hydrolysis reactions and are represented by these equations,

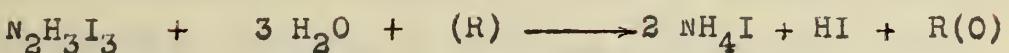


it is quite readily seen that the total iodine in each case as a decomposition product, bears positive electrostatic charges. As both of these equations represent hydrolysis reactions, and as the hydrolysis requires little or no thermic energy to produce chemical reaction, it is quite possible that no internal changes of electrostatic charges take place within the molecule. If this be the case, then the possibility of the total iodine contained in nitrogen iodide bearing positive electrostatic charges is greatly increased.

For the action of reducing agents upon nitrogen iodide,



the chemical reaction produced may be represented thus,



From this equation as in the decomposition of nitrogen iodide by light, it would appear as tho the total iodine contained within the molecule was negatively charged. But in general, reactions of oxidation are always accompanied by a production of thermal energy, this being sufficient to cause an internal electrostatic change of charges within the molecule. On this basis it would still appear reasonable that the total iodine in the original molecule contained all positive charges.

In the work of Noyes and Lyons (1.) and others on the subject of Nitrogen Trichloride, it has been accepted as evident that the total chlorine contained in that compound as being electrostatically charged positive. Nitrogen trichloride on hydrolysis reacts thus,



These two reactions are very similar in nature both indicating that the chlorine and iodine are electrostatically positive in their respective original compounds.

Under the action of reducing agents, the similarity of these two compounds again appears. The chlorine in the trichloride exerting twice the oxidizing power normally associated with that element, the iodine of the iodide producing an

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(1.) refer to J.AM.Chem.Soc. 23, 460, (1901)

(2.) refer to J.AM.Chem.Soc. 39, 896, (1917)



equivalent oxidation power also. Hence judging from this similarity between the actions of the trichloride and the iodide and the reaction products of nitrogen iodide with light, acids, alkalies and the various reducing agents mentioned in the first part of this paper, it seems rather probable that the iodine is combined in the molecule of nitrogen iodide electrostatically positive.



### Experimental.

The nitrogen iodide used in this work was prepared by the method which Chattaway and Orton offer as the most efficient. Mainly thru the action of iodine monochloride upon ammonia. In this reaction, according to the authors, 95% of the iodine appears a nitrogen iodide.

#### Preparation of Iodine Monochloride.

One hundred grams of finely powdered iodine is placed with 300 cc. of hydrochloric acid of sp.gr. I.15 in a porcelain dish and 28 cc. of nitric acid of sp.gr. I.41 is added. This quantity of nitric acid provides sufficient chlorine to convert the iodine to the monochloride. The mixture is warmed on a water-bath to about 40° and continually stirred. The iodine gradually dissolves and the solution becomes orange in color. If the mixture be well stirred and the temperature not allowed to rise above 40°, no chlorine escapes. After the iodine has been completely dissolved, the water-bath is boiled to expel the nitrosyl chloride. With the excess of hydrochloric acid used, the solution is perfectly stable and undergoes no decomposition even on boiling.

#### Preparation of Nitrogen Iodide.

To prepare nitrogen iodide the iodine monochloride is cooled and diluted by adding about three times its bulk of washed, cracked ice. For every 10 grs. of iodine, 100 cc. of strong commercial ammonia of sp.gr. 0.880 are poured over about three times their weight of washed, cracked ice and the cold solution of iodine monochloride slowly run in and the



mixture vigorously stirred during the addition. It is rather important that the monochloride be added to the ammonia, for if the ammonia be added to the monochloride, then iodine is liberated and the yield greatly reduced.

This operation was conducted with light excluded as much as possible and the product was afterward filtered under the same condition, thus greatly reducing decomposition thru that agent. The resulting black amorphous product was filtered thru paper in a large <sup>"</sup>Buchner funnel with suction to decrease the time of filtration as much as possible, (the funnel being previously cooled with crushed ice.) The nitrogen iodide precipitate was then washed with cold dilute ammonia and finally with distilled water at about 4°. Filtration was continued after the last washing until the product was almost dry. The nitrogen iodide thus prepared is of a high degree of purity, but must be used immediately because of its very great instability when dry. Altho nitrogen iodide can be kept without decomposition in an atmosphere of strong ammonia, the same used in this investigation was always freshly prepared to eliminate the uncertainty as to the degree of decomposition.

Crystalline nitrogen iodide can or has been prepared by adjusting the concentrations of the monochloride and ammonia solutions used, in dilute potassium hydroxide. (3%) (1.) Altho no crystalline compound was used in this investigation, the possibility of obtaining the same was demonstrated by using dilute solutions of the iodine monochloride and ammonia, (approx. 0.1N) placing the ammonia above the other component

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(1.) refer to Am.Chem.J. 23, 367, (1900)



in such a manner as to prevent direct mixing of the two components. The ammonia was then covered with a thin layer of paraffin and light excluded completely from the solutions. In the course of a day or so, small reddish or copper colored crystals appeared at the junction of the two solutions. (2.) The crystals formed were very small but under a lens showed the formation of short flat needles and were very brilliant. Under the action of light these crystals lost their brilliancy and on standing directly exposed to sunlight, disappeared completely. This shows that the decomposition products of nitrogen iodide thru the action of light, is composed of volatile components. On repeating the same with the water moist amorphous compound in a closed vessel, it was found that the compound decomposed completely to nitrogen and hydriodic acid; a small amount of free iodine being formed thru hydrolysis from the moisture present. The ratio of the decomposition products thus obtained was not determined quantitatively because of the excellent analyses of the same furnished by Chattaway and Orton. From this decomposition it becomes quite evident that within the molecule, at least three atoms of hydrogen and iodine each, and two of nitrogen are united to form one molecule of nitrogen iodide. If the formula  $N_2H_3I_3$  for nitrogen iodide may be assumed as correct, then the reaction goes as follows,



#### Action of Alkalies on Nitrogen Iodide.

According to Chattaway and Orton, alkaline hydroxides



produce the following reaction with nitrogen iodide,



This affords another method of determining the ratio of the elements in nitrogen iodide. The ratio of ammonia to total iodine was determined as follows. Concentrated sodium hydroxide was added to moist amorphous samples of nitrogen iodide and the ammonia distilled into standard sulfuric acid. The excess being titrated against standard alkali. (methyl orange indicator) The total iodine was then determined by adding 3 grams each of ferrous and ferric sulfates with sufficient dilute sulfuric acid to take up the alkaline hydroxide added, and the iodine distilled over into a strong potassium iodide solution. A current of air was continually bubbled thru the solution to carry the iodine vapors to the receiver. A bent glass tube four feet long and one half an inch in diameter was used to conduct the vapors from the distilling flask into the potassium iodide solution, the container of which and receiver, being at all times kept cold by a salted ice pack. The mouth of the receiver was plugged with glass wool moistened with potassium iodide to collect any iodine vapors that might pass thru the solution without being dissolved. The only rubber connection used in this apparatus was a stopper in the mouth of the distilling flask, and it was protected from the corroding actions of the iodine vapors by a pad of glass wool and a strong current of air introduced thru the stopper. Any iodine being detained within same was washed into the receiver solution after the distillation was completed. The iodine collected was then titrated with a standard sodium thiosulfate solution, starch



(freshly prepared) being the indicator used. The following results were obtained from two portions of nitrogen iodide prepared on different days.

	<u>cc.of</u> <u>0.453N</u> <u>acid</u> <u>used.</u>	<u>cc.of</u> <u>0.522N</u> <u>alkali</u> <u>used.</u>	<u>cc.of</u> <u>N NH<sub>3</sub></u> <u>formed.</u>	<u>cc.of</u> <u>0.1175N</u> <u>Na<sub>2</sub>S<sub>3</sub>O<sub>3</sub></u> <u>used.</u>	<u>cc.of</u> <u>N</u> <u>Iodine.</u>	<u>Nitrogen, Iodine</u> <u>ratio-</u> <u>basing iodine as 3.</u>
1.	25.	9.25	6.496	81.30	9.541	2.048 : 3.
2.	25.	15.30	3.338	42.60	5.011	1.993 : 3.
3.	25.	10.30	6.000	76.55	8.994	2.001 : 3.
4.	25.	13.20	4.435	56.60	6.650	2.007 : 3.
5.	25.	8.40	6.940	88.50	10.398	2.001 : 3.
6.	25.	14.40	3.809	57.20	6.721	1.75 : 3.
7.	25.	10.30	6.000	76.50	8.988	2.002 : 3.
8.	25.	12.55	4.774	61.00	7.167	1.998 : 3.
Average 1.989 : 3.						

From the analytical results obtained, it becomes quite evident that the absolute ratio of the nitrogen to the iodine in nitrogen iodide is 2 : 3. These results check closely with those of Chattaway and Orton and signify that within the molecule, that 2 atoms of nitrogen and 3 of iodine must be associated in some manner.

#### Action of Sulfuric Acid on Nitrogen Iodide.

According to Chattaway and Stevens, the action of acids on nitrogen iodide in general are the same. The side reactions between HI and HOI and the acid being the only products effected by the nature of the acid used.

A sample of the moist amorphous product was treated with approximately  $\text{N}/3 \text{ H}_2\text{SO}_4$ , light being completely excluded. Within half an hour all apparent chemical reaction had reached completion. A small quantity of amorphous iodine precipitate was observed, and judging from the action of the silver ni-



trate solution used, considerable of the iodine acids were formed. An excess of strong sodium hydroxide was then added and the solution warmed slightly. The odor of evolving ammonia became rather strong, hence this process offered a method for determining the amount of ammonium salt formed. No analytical determinations were made on this experiment as it was quite apparent, that knowing the quantity of sulfuric acid added, the free iodine and iodic acids formed could be determined by direct titration while the amount of the ammonium salt formed could be estimated by treatment with an alkaline hydroxide and the ammonia formed distilled off into an acid receiver. The work of Chattaway and Stevens was checked qualitatively as it was deemed unnecessary to repeat the same on a quantitative basis considering the number of analyses of the same they have made and their methods of procedure.

The primary object of this following set of experiments, as stated previous to this, is to endeavor to obtain a compound or compounds similar to nitrogen iodide in structure with the molecule so loaded as to produce a greater stability. The action of iodine in various forms on copper ammonium sulfate was the first of the experiments tried.

#### Preparation of Pure Copper Ammonium Sulfate.

Pure copper ammonium sulfate was prepared by adding an excess of ammonium hydroxide (strong commercial) to a saturated solution of copper sulfate. The copper complex was then crystallized from the mother liquor by adding ethyl alcohol. The size of the crystals obtained depending on the amounts of alcohol added. Crystals two inches in length were obtained



by adding the alcohol at the rate of about ten cc. per day. Although this complex salt of copper is unstable when exposed to atmospheric conditions for any length of time, (reverting back to copper sulfate with the loss of ammonia) it may however be kept in pure form and formula  $\text{Cu} \cdot (\text{NH}_3)_4\text{SO}_4$  by keeping the crystals under a cover of alcohol. The complex salt that was used in the following experiments was kept in crystalline form in the mother liquor until ready for use, filtering and washing same with 95% alcohol before using and then immediately dissolving same in distilled water. In this manner it was possible at all times to be absolutely certain of the formula of the salt being used.

The action of solid crystalline iodine on an aqueous solution of this copper complex was the first of the experiments tried. The iodine seemed to have no effect upon the solution even on standing for one week. A saturated solution of iodine in potassium iodide was then added to the aqueous complex solution. On standing for one week the solution had turned green and a small quantity of a light blue precipitate had appeared. The precipitate was then filtered from the mother liquor and washed with distilled water, dilute alcohol and finally with ether. The compound thus formed contained iodine, ammonia, copper and sulfate. No quantitative analysis being made because of the relatively small quantity of iodine contained as compared to the amount of copper present.

With hopes of producing a similar result, a solution of iodine in carbon tetrachloride was then used but without results. The solution tendency of the iodine in its solvent seeming to exceed the chemical activity of the complex



solution.

A solution of iodine in benzene was then used in place of the carbon tetrachloride solution but still no chemical reaction could be induced.

On repeating the same with iodine dissolved in ether, somewhat better results were obtained, but due to the volatility of the solvent it was rather difficult to keep the iodine solution at any particular concentration. The ether solution of iodine yielding a small quantity of a greenish blue precipitate which contained iodine, ammonia, copper and sulfate.

A solution of iodine dissolved in alcohol was found to produce the best results but even at best many difficulties were encountered. When iodine in alcoholic solution is slowly added to an aqueous solution of the copper complex, the complex solution takes up considerable of the iodine, the solution changing in color from blue to green. Whether this change in color is due to chemical reaction or a blending of the iodine color and the blue to form a green, or a combination of both, could never be determined. If this solution be allowed to stand for a day or so, a greenish blue precipitate appears to coat the bottom of the container. After the precipitate is filtered from the mother liquor the solution reverts back to the characteristic blue color. If more iodine be added it is precipitated in the amorphous state. If the green solution be concentrated by boiling, then a dark green precipitate is obtained in small quantity and the solution reverts back to copper sulfate. At all times considerable iodoform is obtained and continues to be produced as long as both of its components



(alcohol and iodine) are present. This formation of iodoform seems to take place equally as well in cold, warm and hot solutions. The greenish blue product containing iodine, ammonia, copper and sulfate while the latter contained only iodine, copper and sulfate. In general of the salts obtained by boiling to concentrate the mother liquor, few were found to contain ammonia and then only in very small quantity. The procedure was then repeated in the following manner so as to obtain a sufficiency of the product to analyse quantitatively.

About fifty grams of freshly filtered copper ammonium sulfate was dissolved in just enough water to dissolve it completely. A concentrated solution of iodine in alcohol was then added 5 cc. at a time between two minute intervals of severe shaking. The iodine was added until it precipitated in the amorphous state. The solution was then filtered and the filtrate was green in color. The same was then warmed gently to drive off most of the alcohol. Simultaneously with the warming a bluish white flocculent precipitate appeared. On cooling the solution changed from green back to the characteristic complex blue. The precipitate obtained was then filtered off, washed and dried giving a final yield of barely half a gram. On drying the product was found to be of a pale blue color and contained the following elements, copper, ammonia and iodine, the latter being present in considerable quantity. On repeating the same procedure and endeavoring to produce conditions similar to those under which the first product was obtained, quite different results were obtained. This time the product appeared to form on the bottom of the container used in a thin layer, was of a greenish blue color, contained



copper, iodine, ammonia and sulfate. This same procedure was twice repeated and each time a product different in nature from the first was obtained. On repeating the same again, iodoform was produced with such ease and rapidity that no precipitate was obtained.

The effect of temperature on the method of procedure was then determined. At  $0^{\circ}$  it was very difficult to get the copper complex solution to take up iodine so the temperature was raised to  $40^{\circ}$ . At this temperature a variable product was obtained both in color and qualitative composition, the iodoform reaction causing considerable difficulty at all times. The reaction was then tried at  $80^{\circ}$  but without any better results. The characteristic green solution obtained when iodine is added to the aqueous complex solution, was then concentrated rapidly by vigorous boiling. Under these conditions a dark green precipitate was obtained corresponding yellow green shade 2. (1.)

This product was practically insoluble in cold water and only very slightly so in that solvent when hot. It was readily soluble in dilute acids and alkalies and acids and qualitatively was composed of iodine, copper, a small amount of sulfate and a trace of ammonia. On standing for a few days this substance lost its trace of ammonia and became very dark green in color. Analysis of the decomposed product gave a ratio of 1 : 1 between the iodine and copper present.

The possibility of using copper ammonium hydroxide in

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(1.) refer to Mulliken, vol. 2 color schedule

"Identification of Pure Organic Compounds".



place of the sulfate complex was then tried. Considerable difficulty was encountered in this case in preventing the breaking down of this complex into copper oxide. In only one case was a small quantity of product obtained. The compound being of a pale blue color.

On the whole this method of attack seemed to be a failure and offered no apparent indication of serving the primary purpose. Of the various products obtained, the author succeeded in preparing seven different colored compounds, the colors varying from light blue tint 2, thru the blue and yellow greens to dark yellow green of shade 2. The color of the product varying (1.) with the temperature at which it was prepared, light blue and blue greens being produced at the lower temperatures ( $20-40^{\circ}$ ) and yellow green to dark green at higher temperatures ( $60-100^{\circ}$ )

As this procedure apparently offered no solution to the problem in question, further research was conducted in a different channel.

From the preceding experiments it is quite apparent that the copper ammonium complex is chemically active toward iodine, and as nitrogen iodide can be prepared very efficiently thru the action of iodine monochloride on ammonia, there should be a possibility of chemical reaction between the iodine monochloride and the complex salt. A small portion of an aqueous solution of the copper complex cooled by icing was added to iced iodine monochloride. (conditions being maintained the same as in the preparation of nitrogen iodide) On adding the one

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component to the other a black amorphous precipitate was obtained. The addition of the one solution to the other being accompanied by the evolution of considerable nitrogen gas. On drying the black product obtained, it was found to be non-explosive and containing considerable iodine, some copper and little ammonia. The dried compound being very unstable, iodine vapors continually evolving. The compound was then prepared at minus 15° thru the use of salted ice, but still considerable nitrogen was evolved in the procedure. Analysis of the compound prepared at this temperature gave variable results the ratio of the copper to iodine varying slightly below unity while the ammonia iodine ratio indicated a possibility of 2 : 3. In order to prepare this compound in a higher degree of purity, the components were slowly mixed with constant stirring in a tube about two inches in diameter surrounded by a saturated solution of calcium chloride of formula  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and finely chipped ice in a Dewar tube. The evolution of nitrogen gas was still apparent but greatly reduced at this temperature of minus 30°. In order to obtain the product free from an excess of one of the components, filtration seemed to offer the only possible solution. To filter this compound required both low temperature and speed so it became necessary to devise a super-cooled filtering apparatus.

A four inch funnel with a long wide stem was placed in a six inch funnel with a shortened stem by means of a rubber stopper. This making it possible to cool the inner funnel with cracked ice and calcium chloride solution. In order to facilitate speed in filtering a Gooch filter plate was placed in the



inner funnel and covered with coarse filter paper. By means of an apparatus of this kind the low temperature could still be maintained thruout the operation and the rate of filtration increased by suction.

Owing to the peculiar nature of the product, this filtering device failed to serve the purpose. The compound on decomposing gives off nitrogen, free iodine and a gelatinous precipitate of copper which so completely clogged the pores of the filter and slowed up filtration to such a degree that the filtrate froze in the stem of the funnel, hence completely restricting all possibility of filtration.

It had been previously noticed that a greater portion of the precipitate settled to the bottom of the container as soon as it was formed. This incident suggested the possibility of decantation. In preparing the compound after a quantity of the copper ammonium sulfate which had been estimated as sufficient was added, the container was at once filled with cold distilled water. But on allowing this diluted mixture to stand in the freezing bath for five minutes, it was noticed that the product that had settled to the bottom was encased in a mass of solid ice. The unfrozen solution above (still containing some of the product) could then be poured off and more water added. On adding water to this iced mass of precipitate most of the ice was melted in cooling the water, at the same time diluting the remaining impurities. The mixture was then allowed to freeze again and the process repeated. In this manner all of the remaining impurities could be removed and as a result, as pure a product as could be prepared at minus 30° was ob-



tained. In analysing this substance the same methods used in determining the ammonia iodine ratio in nitrogen iodide were employed. The copper being determined by precipitation as the sulfide from hot sulfuric acid solution, then dissolved in nitric acid which was then replaced by sulfuric acid. The copper sulfate was then dissolved in water, the excess acid neutralized with sodium bicarbonate, then made slightly acid with acetic acid and titrated against the same sodium thiosulfate solution used in determining the iodine present. Of a series of twelve determinations the best results obtained are given.

No. of sample	1.	2.	3.	4.
cc. of 0.459 <i>N</i> acid used.	35.00	35.00	35.00	35.00
cc. of 0.497 <i>N</i> alkali used	31.50	31.45	14.80	12.10
cc. of N-NH <sub>3</sub>	0.790	0.815	4.120	5.461
cc. of 0.073 <i>N</i> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> used	13.75	15.50	82.50	104.50
cc. of N-I.	1.003	1.131	6.032	7.628
cc. of 0.073 <i>N</i> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> used.	13.40	15.30	82.00	104.15
cc. of N-Cu.	0.978	1.116	5.986	7.603

Cu-NH<sub>3</sub>-I ratio; .97-1.27-1 .98-1.38-1 .97-1.46-1 .996-1.39-1.

Average ratios: Cu.0.98 - NH<sub>3</sub>, 1.38 - I, 1.0

Attempts were also made to obtain the sample in the anhydrous form by drying over phosphorous pentoxide but were met with no success because decomposition always took place before the compound had become dry.



From the above analyses it may be seen that the ratios suggest the formula  $\text{Cu}_2(\text{NH}_3)_3\text{I}_2$  and also that considerable nitrogen loss still occurred during the preparation of the compound.

In order to decrease this loss of nitrogen as much as possible, a freezing mixture of carbon dioxide snow and ether was used in place of the cracked ice and calcium chloride. With this mixture a temperature of minus  $80^{\circ}$  is possible. The compound was prepared and washed by the combination method of decantation and freezing as was used in making the substance at minus  $30^{\circ}$ . The following results give the relative analysis of the compound obtained.

<u>No. of sample</u>	<u>1.</u>	<u>2.</u>	<u>3.</u>	<u>4.</u>
<u>cc. of 0.459 N acid used</u>	25.00	25.00	25.00	25.00
<u>cc. of 0.497 N alkali used</u>	10.40	1.25	1.90	2.55
<u>cc. of N-NH<sub>3</sub></u>	6.306	10.854	10.531	10.208
<u>cc. of 0.1264 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> used</u>	25.50	43.60	42.50	41.20
<u>cc. of N-I.</u>	3.223	5.511	5.372	5.207
<u>cc. of 0.1264 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> used</u>	16.65	28.50	27.50	26.50
<u>cc. of N-Cu.</u>	3.104	3.602	3.475	3.349

<u>Ratios:</u>	<u>Cu.</u>	<u>:</u>	<u>NH<sub>3</sub></u>	<u>:</u>	<u>I.</u>
1.	1.958		5.87		3.00
2.	1.960		5.91		3.00
3.	1.940		5.88		3.00
4.	1.930		5.88		3.00
<u>Average</u>	<u>1.947</u>	<u>:</u>	<u>5.885</u>	<u>:</u>	<u>3.00</u>

Judging from the above results, it would appear that the absolute ratios of the components are 2 : 6 : 3, making the



simplest formula possible  $\text{Cu}_2(\text{NH}_3)_6\text{I}_3$ . But this however is quite different from that of the compound obtained at minus 30°, containing both higher ammonia and iodine content.

On treatment of a portion of this frozen product with dilute ammonium hydroxide (approx. N.1) a blue filtrate resembling the copper ammonium sulfate complex in color and a black amorphous precipitate was obtained. On drying this precipitate its actions were very similar to nitrogen iodide. Of a portion of this precipitate washed and treated as was the previous nitrogen iodide, <sup>When</sup> analysed, the following results were obtained.

No.	cc. of 0.459N acid used.	cc. of 0.497N alkali used.	cc. of <u>N</u> $\text{NH}_3$	cc. of 0.073N $\text{Na}_2\text{S}_2\text{O}_3$ used.	cc. of <u>N</u> I.	Ratio of nitrogen to iodine basing iodine as 3.
1.	10.00	6.30	1.51	31.05	2.266	1.99 : 3.
2.	10.00	3.75	1.86	38.85	2.856	1.96 : 3.

From these results it appears as though the compound formed really is nitrogen iodide, the nitrogen and iodine ratios corresponding very closely to the results of previous analyses obtained.

On treatment of a portion of this compound prepared at minus 80° with N95 sulfuric acid, a black amorphous residue and a solution with a faint iodine color was obtained. A portion of this solution was then treated with silver nitrate and the presence of iodic acids was confirmed. The black precipitate was then analysed and found to be composed totally of amorphous iodine. An estimation of the quantity of iodic acids was then made. A fresh portion of the frozen compound was treated under the same conditions as before and the iodine precipitate



filtered off, dissolved in potassium iodide solution and titrated with a standard sodium thiosulphate solution. The titrated solution was then added to the filtrate and the total iodine determined by the regular method. About 7 % of iodic acids was found to have been present. This would indicate that half of the iodine in the initial compound was combined as positive and the other half as negatively charged. In order to further determine the nature of this compound produced, considerably more data would have to be obtained and the problem would then have to be viewed from more than one point of view.

It does, however, appear that if the nature of these compounds produced thru this method of attack, was clearly established, the results obtained would throw much light upon the structure of and the valence of iodine in nitrogen iodide. When finally these compounds obtained thru the action of the copper complex upon iodine monochloride are thoroughly understood and controlled, then by analogous reasoning, the complexes of silver, cadmium, zinc, nickel and cobalt with ammonia, should produce salts with iodine monochloride whose properties could in turn be predicted beforehand. Hence with such a quantity of accumulated material which, of course, would have to be upheld by analytical data, the problem of the valence of iodine in nitrogen iodide would undoubtedly be much clearer.

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